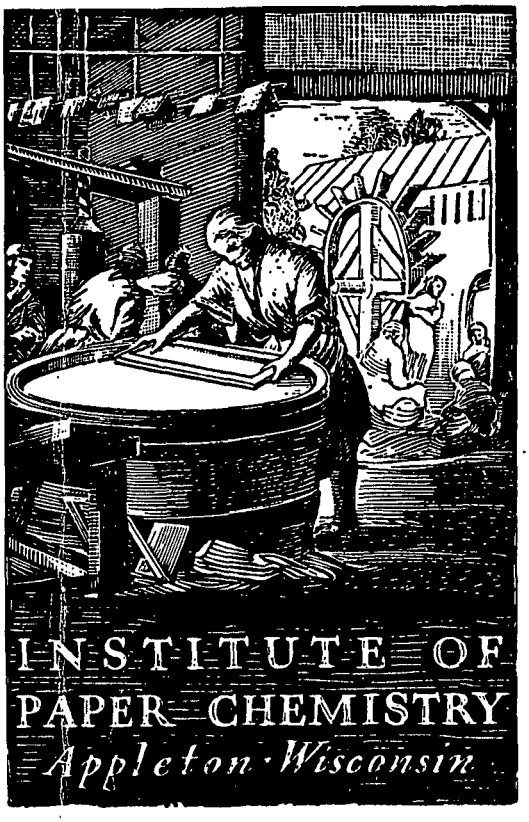

MAXIMIZATION OF SOAP YIELD IN ALKALINE PULPING

Project 3267

Report One

A Progress Report

to

MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY

March 15, 1976

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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ABSTRACT

Partially concentrated black liquors were procured from five kraft mills and were analyzed for extractable, crude tall oil (CTO). Due to the small number of samples the results were statistically insensitive to the relative efficiencies from mill-to-mill. Aliquots of the liquors which had been stored for as long as a year were unchanged in the amount and composition of CTO. An isolated sample of black liquor was exposed repeatedly to air at room temperature, but no change was observed in the CTO or its composition.

Liquors were analyzed by conventional chemical methods and by a combination of chemical and ion-exchange material, DEAE-Sephadex (a diethylaminoethyl ether of a cross-linked dextran). The DEAE-Sephadex was preferred for most analyses of CTO.

Laboratory kraft cooks of loblolly pine chips (and aspen as a resin-free control) were used to evaluate the production of skimmable soap under controlled conditions. Although precipitated soap formed skimmable scums in all cooks except the aspen and extractive-free pine chips, cooks with resin acid:fatty acid ratios of >3:1 retained somewhat higher levels of CTO in solutions than normal cooks. The CTO from fiberized chip washings was similar to other fractions of CTO except that the abietic acid:dehydroabietic acid ratio was very much smaller and resembled that from CTO obtained in oxygen-alkali pulping of pine. These observations are consistent with the known sensitivity of abietic acid to oxidation.

Preliminary experiments with high performance liquid chromatography were conducted with tall oil components, chiefly fatty and resin acids. A Varian

Model 8500 liquid chromatograph with a Perkin-Elmer Model LC-55 variable wavelength spectrophotometric detector were used with assorted columns. The results indicated that the separation of tall oil components may be efficient and reasonably rapid, but the spectrophotometric detector limits the sensitivity and versatility of the method. For the evaluation of tall oil mixtures it is obvious that a universal type of detector (such as a moving wire type) is required.

STATEMENT OF THE PROBLEM

In the development of kraft recovery practices it was learned empirically that when fresh southern pinewood was pulped by the kraft (sulfate) process, maximum yields of soap skimmings are obtained if the black liquor is skimmed from a partially concentrated liquor of from 25-27% solids held in a tank at an elevated temperature for approxiately one hour. The conditions necessary for maximized soap skimmings are operative when fresh southern pinewood is pulped by the kraft process, but such conditions no longer exist at a large number of kraft mills. For a variety of reasons many kraft mills have introduced parameters into their mill practice which cause the ideal conditions necessary for optimized soap skimmings to depart from the permitted range. Such parameters include use of hardwood in the kraft furnish (pulped together or separately with combined black liquors), outside chip storage, long-term roundwood storage, use of decayed and inferior wood, use of bark-containing and whole wood chips, use of resin-soaked chips, etc. As a result, most mills are experiencing much lower tall oil recoveries. A detailed account of the subject was reported by Bolger and Hopfenberg in 1965 (1).

OBJECTIVES

As set forth in our original proposal, the objectives of the experimental program of this Project are:

1. To determine the composition of kraft black liquors under conditions of low and high yields of soap skimmings.
2. To relate the yields of soap to mill operational parameters.
3. To establish empirically the effects of changes in operational parameters on maximization of the yield of soaps.
4. To make a theoretical analysis of the solubility behavior of low and high yield soap systems and establish how the implications of this analysis can be used to maximize the yield of tall oil in a given kraft mill system.

RESEARCH PROGRAM

The initial phase of our research program was concerned with objectives 1 and 2, and our experience to date is covered by the present report. Chapter I is concerned with the determination of crude tall oil in black liquors from typical commercial operations and of skimmable soaps from laboratory kraft cooks. Chapter II describes our experience with the application of high performance liquid chromatography to the analysis of tall oil and its components.

CHAPTER I

THE DETERMINATION OF CRUDE TALL OIL IN BLACK LIQUORS FROM TYPICAL COMMERCIAL OPERATIONS

Several purchasers of crude tall oil were canvassed to obtain a consensus on very efficient tall oil soap recovery mills and on very inefficient tall oil soap recovery mills. The information obtained led to a choice of three "efficient" and two "inefficient" soap recovery mills. These mills were visited, and arrangements were made to obtain samples of partially concentrated black liquors to and from the soap-skimmers.

RESULTS AND DISCUSSION

Recovery of Crude Tall Oil (CTO) from Commercial Black Liquors

Partially concentrated black liquors were procured from the five kraft mills. As shown in Table I, samples to-the-soap skimmer and from-the-soap skimmer were analyzed by the method of Saltsman and Kuiken (2). The results (Table I) revealed a considerable range in the apparent efficiency of the skimming operation, but the residual (extractable) CTO in the from-the-skimmer liquor indicated that relatively small additional amounts of CTO would be recoverable as skimmable soaps. This was evident from the relatively small proportion of soap scum which formed on some of the from-the-skimmer liquor samples. In accord with the observations of Bolger and Hopfenberg (1), most of the CTO soaps present in skimmed liquor are dissolved in the liquor and, hence, require some additive to precipitate the material as a recoverable soap. However, practical and economic limitations usually have prevented the use of such agents and devices in industrial practice to recover additional CTO from skimmed liquors.

TABLE I

CRUDE TALL OIL (CTO) CONTENTS OF COMMERCIAL BLACK LIQUORS

Symbol	Company, location of mill	Solids Content % o.d. solids, weight basis of liquor		CTO, % o.d. liquor solids[a]		Soaps Collected from Black Liquors			
						From Liquor to Skimmer		From Liquor – From Skimmer	
		To Skimmer	From Skimmer	To Skimmer	From Skimmer	o.d. Solids in Soap, %	CTO, % o.d. solids	o.d. Solids in Soap, %	CTO, % o.d. solids
TH	Thilmany Pulp and Paper Co. Kaukauna, WI	28.7	31.7	1.24	0.39 (0.128)	61.9	72.9	69.5	79.5
OI	Owens-Illinois, Inc. Valdosta, GA	28.0	28.7	1.76	0.48 (0.138)				
BR	Brunswick Pulp and Paper Co. Brunswick, GA	27.2	27.5	1.83	0.74 (0.204)	61.3	75.3	65.9	79.7
SC	Scott Paper Co. Mobile, AL	18.0	23.4 19.3 22.5	2.13	0.55 (0.129) 0.36				
HM	Hammermill Paper Co. Selma, AL	21.3	20.9	1.99	0.78 (0.163)	62.3	72.4	62.4	65.6

[a] Numbers in parentheses are CTO expressed as weight-percent of black liquor.

As shown in Table I, columns 7-10, to-the-skimmer liquors and, in some cases, from-the-skimmer liquors produced soap scums which were collected and analyzed, but no attempt was made to determine yields of skimmed soaps. Considering the phase characteristics of these soaps, they were remarkably uniform in composition, and appeared to be similar to that generally reported for soap skimmings which contain 3-15% black liquor solids, 30-40% water, and 45-55% CTO.

Composition of CTO Obtained from Commercial Black Liquors

A. Chemical Fractionation

The CTO was separated into three classes of material, neutral (unsaponifiables), fatty acids, and resin acids, by conventional chemical procedures (3-5). The results are shown in Table II. Although the relative amounts of the three classes of material varied somewhat, the compositions of the several CTO samples were typical of those generally reported. The relative amounts of neutral and resin acids were slightly larger in the from-the-skimmer liquors than in the to-the-skimmer liquors. This observation suggests that the neutrals and the resin acid salts are slightly more soluble in the black liquor than are the salts of the fatty acids. (Experiments have been planned to test this observation; see p. 24.

B. Fractionation on DEAE-Sephadex

An improved fractionation of CTO by means of an ion-exchange material, DEAE-Sephadex, was described by Zinkel and Rowe (6-7). The results for selected samples of CTO are listed in Table III. A comparison of the analyses obtained by the chemical and the DEAE-Sephadex methods indicated that the methods are probably equally reliable. Because the manipulations of the DEAE-Sephadex procedure are somewhat simpler than those of the chemical procedure, it was chosen for most analyses of tall oil. In the last column the unaccounted-for materials are listed as a loss-by-difference and may represent substances other than the normal unsaponifiables, fatty acids, and resin acids.

TABLE II

FRACTIONATION BY CHEMICAL METHODS OF CTO ISOLATED FROM COMMERCIAL BLACK LIQUORS

Company Symbol	To/From Skimmer	CTO, % o.d. solids	Composition as % CTO[a] Unsap. (neutrals)	Fatty Acids	Resin Acids	Loss (by diff.)
OI	To	1.26	11.6	33.2	44.5	10.7
	From	0.39	15.8	23.0	49.1	12.1
TH	To	1.63	9.8	42.1	38.2	9.9
	From	0.48	13.0	34.1	53.6	--
BR	To	1.83	9.6	41.2	38.2	11.0
	From	0.74	11.4	38.3	44.5	5.8
HM	To	1.98	9.3	51.5	35.5	3.7
	From	0.78	19.6	38.1	36.3	6.0
SC	To	2.12	15.2	44.8	30.6	9.4
	From	0.54	16.1			

[a]Relative percentage based on CTO.

TABLE III

FRACTIONATION OF CTO ON DEAE-SEPHADEX

Company Symbol	Sample	Composition as % CTO[a] Neutrals	Total Acids	Fatty Acids	Resin Acids	Loss, by diff.
TH	Soap (to skimmer)	12.1	87.7	--	--	--
SC	Liquor from skimmer	16.1	83.9	--	--	--
SC	Liquor to skimmer	14.8 (15.2)	85.2	44.8 (44.8)	30.6 (30.7)	9.8 (9.3)
HM	Liquor to skimmer	9.4 (9.3)	89.2	49.7 (51.5)	30.2 (35.5)	9.3 (3.7)
HM	Liquor from skimmer	17.9 (19.6)	80.8	40.5 (38.1)	35.9 (36.3)	4.4 (6.0)
BR	Soap (to skimmer)	13.3	86.7	44.7	35.2	6.8

[a]The numbers in parentheses were determined by conventional chemical methods and were listed, also, in Table II.

Analysis of Tall Oil Fractions by Gas Chromatography

The compositions of the fatty and resin acids obtained from tall oil were determined by gas chromatography. As shown in Table IV, the compositions were typical of recovered tall oils with oleic and linoleic acids dominant in the fatty acids, and pimaric, abietic, and dehydroabietic the dominant resin acids.

CTO Content of Stored Black Liquor

In order to determine whether or not the tall oil contents of black liquors decline when the liquors are stored, aliquot samples of black liquor were analyzed after storage at room temperature. The results, as listed in Table V, show that little if any significant losses occurred over a period of nearly a year. Additional aliquots are available and will be analyzed to reinforce the conclusion that storage of black liquor under anaerobic conditions is not detrimental to its tall oil content. It may be noteworthy that all stored liquor samples were covered with a scum of precipitated soap. The separation of phases requires that analyses be performed on the entire contents of each aliquot in order to assure comparable results.

Possible Loss of Tall Oil Upon Exposure of Black Liquor to Air

A stream of air was bubbled through a column of black liquor at 15-minute intervals over a period of three hours. The tall oil recovered was 1.58% based on liquor solids in contrast to 1.12% in a separate aliquot without aeration. The increase in extractable tall oil rather than a possible decrease may reflect experimental error, but, in this case, exposure to air was not deleterious.

Conclusions from Commercial Black Liquor Studies

An evaluation of all the results obtained on the to-the-skimmer and from-the-skimmer black liquors from the three "efficient" and two "nonefficient"

TABLE IV

RELATIVE COMPOSITION (%) OF TALL OIL FATTY ACIDS
AND RESIN ACIDS BY GAS CHROMATOGRAPHY
ANALYZED AS METHYL ESTERS

	Company Symbol			
	HM		OI	TH
Fatty Acids, % CTO	To Skimmer	From Skimmer	To Skimmer	Soap (to Skimmer)
Unknown	3.7	9.9	8.0	3.7
Palmitic	8.7	9.7	8.9	12.8
Palmitoleic	1.7	1.7	3.4	1.5
Stearic	3.5	1.7	1.8	--
Oleic	41.0	38.2	38.3	40.0
Linoleic	30.0	30.8	28.8	30.3
Unknown[a]	9.5	10.0	10.5	9.0
Resin Acids, % CTO				
Unknown	2.6	1.1		
Pimaric	17.8	9.4		
Dihydroabietic	4.2	2.3		
Levopimaric / Palustric	13.1	9.3		
Isopimaric	<1	<1		
Abietic	11.9	46.0		
Dehydroabietic	49.6	30.0		
Neoabietic	2.2	<1		

[a]Includes all fatty acids $\geq C_{20}$ along with a trace (<1%) of linolenic acid.

TABLE V

EXTRACTABLE CTO FROM COMMERCIAL BLACK LIQUORS AFTER STORAGE[a]

Experiment	1		2		3		4		5	
Company	Date Analyzed	CTO % o.d. Solids	Date Analyzed	CTO % o.d. Solids	Date Analyzed	CTO % o.d. Solids	Date Analyzed	CTO % o.d. Solids	Date Analyzed	CTO, %
Thilmany	3-21-75	1.63	5-7-75	1.76	6-30-75	2.12	10-17-75	1.81	2-2-76	1.55
Owens-Illinois	3-26-75	1.26					10-17-75	1.90	1-30-76	1.51
Scott					6-9-75	2.12	10-21-75	1.54 1.97	2-4-76	2.30
Brunswick	3-25-75	1.83					10-20-75	2.03	2-2-76	1.15
Hammermill	4-15-75	1.98					10-20-75	2.45	2-3-76	1.68

[a]Only to-the-skimmer liquors were analyzed after storage.

mills demonstrated that the labelling of kraft mills as "efficient" or "nonefficient" tall oil soap skimmers must be on a statistical basis, because we found that "nonefficient" mills can be extremely efficient on a particular day and vice versa. Accordingly, it was decided that for succeeding experiments we would employ black liquors prepared in our pulp lab under varying conditions of rosin acid and fatty acid content.

LABORATORY KRAFT COOKS OF LOBLOLLY PINE AND ASPEN TO ATTEMPT TO DETERMINE TALL OIL POTENTIAL. FIRST SERIES

Six kraft cooks of loblolly pine chips and one of aspen chips were performed simultaneously in half-liter, stainless steel digesters. At the end of the schedule the digesters were cooled to approximately 90°C, were opened, and the liquor was decanted from the chips through a fine mesh, stainless steel screen. The cooked chips were placed in a Waring Blendor with approximately 2 liters of hot water and fiberized mechanically. The pulp slurry was transferred to a coarse sintered glass funnel, was washed with water, pressed under a rubber sheet, and reserved for a yield determination.

The decanted liquor was allowed to stand at room temperature overnight, was separated into an upper and lower fraction, and CTO was determined for each fraction.

The yields of total CTO, skimmable soap, and dissolved CTO were estimated by the method of Saltzman and Kuiken (2). The results are summarized in Table VI. A soap scum had formed in all except the aspen liquor (column Ⓐ). By determining the CTO in the upper and lower fractions of the black liquor, the yield of skimmable soap was defined simply as the difference between the total CTO and that dissolved in the liquor. Except in the case of aspen, skimmable soap was measured for all

TABLE VI

LABORATORY KRAFT COOKS OF ASPEN AND LOBLOLLY PINE CHIPS. FIRST SERIES

Each digester was charged with 85 g o.d. wood (73 g of aspen); at 22% alkalinity (Na_2O), 30% sulfidity, liquor-to-wood ratio, 3.75:1, and cooked at 170°C at an H factor of 1500 (85 to 170° in 120 min, 65 min at 170°)

Digester	(A)	(A+B)	(B)	(C)	(D)	(E)
Sample	Aspen	Aspen + Pine Liquors	Pine Control	Pine Control	Pine + 1.5% Fatty Acids	Pine + 1.5% Resin Acids
Yield of pulp, % o.d. wood	46.4	--	48.5	49.7	52.3	50.8
Kappa number	13.4	--	40.6	45.8	71.8	68.4
Solids content of black liquor, % by weight	15.3	15.9	16.9	16.4	16.0	15.6
Crude tall oil (CTO) by extraction of lower fraction, % basis of black liquor solids (BLS)	0.51	0.91	0.84	0.65	0.79	1.11
CTO solubility, g/100 g black liquor	0.077[a]	0.142	0.142	0.107	0.126	0.173
CTO as skimmable soap, % o.d. wood	--	0.17	0.51	0.72	2.22	1.18
Total CTO by extraction, % o.d. wood	0.43	0.37	1.19	1.25	2.83	2.07

[a] This concentration is less than the solubility.

cooks including a synthetic liquor (column Ⓐ + Ⓑ) composed of a mixture of aspen liquor Ⓐ and loblolly pine liquor Ⓑ. Even so, the amount of skimmable soap was less than the undiluted loblolly pine control Ⓑ.

The data in both columns Ⓑ and Ⓒ, Table VI, were obtained for unextracted loblolly pine (controls) and are similar. In columns Ⓓ and Ⓔ the unextracted wood was spiked with 1.5% each of tall oil fatty acids and resin acids (rosin), respectively. As might be expected, additional skimmable soap was formed. The presence of an disproportionately large amount of resin acids (column Ⓔ) did not hinder the formation of skimmable soap. However, the ratio of fatty acids to resin acids may still have been favorable for the formation of a floating precipitate (see Table VII).

Based on these experiments the solubility of tall oil soaps (sodium salts of fatty and resin acids) appeared to be the limiting factor on the formation of a skimmable soap scum. By this definition the solubility of CTO soaps was 0.11-0.17 g per 100 g of black liquor (digester strength). This would readily account for the absence of a soap scum on liquor Ⓐ where the concentration was only 0.077 g per 100 g of liquor. Similar values were obtained for the commercial black liquors (see column 6, Table I). Although the commercial liquors contained nearly twice the concentration of solids of the laboratory liquors, the potential recovery of skimmable soap, on a unit volume basis, from the more dilute laboratory liquors was undiminished. The total yield of tall oil, of course, would increase as the solids content of the liquor was increased before skimming.

Bolger and Hopfenberg (1) reported solubilities of tall oil soaps which were similar to those in these studies (Project 3267). However, they demonstrated that possibly more than half the apparently soluble tall oil soaps could be coagulated and skimmed by suitable additives or by the introduction of air as very

fine bubbles. They concluded that a portion of the apparently soluble tall oil in the liquor from most skimming operations is in the form of a colloidal dispersion and capable of being precipitated and recovered while the remainder, 0.3% on a solids basis, is in true solution and cannot be recovered.

TABLE VII

FRACTIONATION OF CTO FROM SELECTED LABORATORY KRAFT COOKS OF LOBLOLLY PINE. FIRST SERIES

Black Liquor Sample and Description of Experiment	CTO Basis o.d. wood, %	Fractions as % CTO[a]		
		Neutrals (Unsap.)	Fatty Acids (as Methyl Esters)	Resin Acids
(C) Pine chips, control				
Upper fraction	0.42	12.2	51.8	34.8
Lower fraction	0.53	25.5	77[b]	
(D) Pine chips + 1.5% fatty acids				
Upper fraction	1.26	13.1	62.2	18.8
Lower fraction	0.61	17.1	45.4	22.4
(E) Pine chips + 1.5% resin acids				
Upper fraction	0.74	9.1	41.5	35.4
Lower fraction	0.89	4.6	25.2	32.2

[a] Experimental error and scatter due to unknown CTO components.
[b] Combined fatty and resin acids.

Fractionation of CTO from Laboratory Kraft Cooks and Analysis by Gas Chromatography. First Series

Some lots of the CTO produced in this series of kraft cooks were selected for fractionation and analysis; the results are listed in Tables VII and VIII. The proportion of fatty acids (Table VII) appeared to be somewhat higher in the upper fractions of black liquor than in the lower fractions, but the reverse pattern for resin acids was less obvious. At present, no further work has been planned to explore this observation.

TABLE VIII

GAS CHROMATOGRAPHIC ANALYSIS (RELATIVE) OF TALL OIL FATTY ACIDS AND RESIN ACIDS AS METHYL ESTERS FROM LABORATORY KRAFT COOKS. FIRST SERIES

Fatty Acid Derivatives[a]	Retention Time, min	Composition, percent by weight based on fraction analyzed: C Control, upper fract.	D, upper fract.	E, upper fract.	Rosin 63-30 WG[b]	Rosin 63-10 WG[b]	Acintol SPR Fatty Acids[c]	Extractives of Loblolly Pine[d]
C_{16}	--	<1						1.5
Palmitic	4.7	9.2	5.2	8.6			1.8	8.1
Palmitoleic	5.7	1.8	1.7	2.5			1.0	2.0
C_{17}	6.2-6.3	<1	<1	<1			<1	<1
Unknown	7.6-7.6	<1	<1	<1			--	<1
Stearic	8.4	2.6	2.8	3.3			2.1	2.9
Oleic	9.9	44.8	46.0	40.3			48.4	39.6
C_{19}	11.2	<1	1.1	1.0			<1	1.2
Linoleic	12.7	23.4	26.4	22.9			36.6	31.2
C_{20}	14.5	1.2	2.1	2.0			3.0	5.0
Linolenic	17.6	5.4	6.4	5.6			3.8	1.6
Unknown	19.5	5.9	4.7	5.7			2.7	1.1
Unknown	20.6							
Unknown	22.5-22.7	1.4	1.5	1.9				
C_{22}	25.4	3.1	2.2	4.2				5.1
Resin Acid Derivatives[a]								
(Fatty acids)	0.0-12.0	1.3	2.4	<1	2.4	2.0		2.2
Unknown	13.2-13.3	<1	<1	<1				--
Tetrahydroabietic	14.3-14.5	<1	1.3	<1	<1	<1		<1
Pimaric	16.1-16.3	10.4	10.4	7.9	3.8	3.6		9.3
Sandaracopimaric	18.0-18.2	1.9	1.6	2.2	2.1	2.1		2.0
Dihydroabietic	20.2-20.5	<1	<1	<1	<1	<1		<1
Palustric + Levopimaric	22.1-22.3	<1	<1	2.0	7.6	6.5		2.5
Isopimaric	23.6-23.8	3.6	2.7	10.6	15.7	16.0		3.3
Unknown	28.3-28.5	<1	<1	1.2	1.1	<1		1.4
Abietic	34.5-34.9	34.0	34.4	42.3	49.6	48.1		46.9
Dehydroabietic	38.2-38.6	47.6	47.6	32.7	15.7	17.0		33.0
Unknown	41.0	--	--	<1	1.5	1.3		<1
Neoabietic	44.9-45.3	<1	1.3	<1	<1	<1		<1

[a] Presumptive identification by retention time and comparison with authentic reference compounds.
[b] Commercial tall oil rosin samples labelled "from Valdosta."
[c] Refined tall oil fatty acids from Arizona Chemical Co., New York, New York.
[d] Acetone extractives after saponification and fractionation.

Analytical results by GLC of the acid fractions (as methyl esters) of CTO samples along with those of reference materials are listed in Table VIII. Throughout the series there were no obvious abnormalities. The main fatty acids were oleic and linoleic and the main resin acids were abietic and dehydroabietic along with lesser amounts of pimaric and palustric.

LABORATORY KRAFT COOKS OF LOBLOLLY PINE CHIPS. SECOND SERIES

The results of the first series of experimental kraft cooks produced evidence that when resin acids were added to unextracted chips (Table VI, column (E)), the solubility of CTO in the black liquor was increased somewhat. In order to verify this observation and to attempt a summative analysis of all the CTO in the system, a second series of kraft cooks was performed.

As listed in Table IX, unextracted, extracted, and "spiked" chips were cooked by the same schedule as in the first series. However, the results of the two cooks are not comparable because in the first series only the decanted liquor was analyzed and, in the second series, both the black liquor and the fiberized chip washings (FCW) were analyzed. In all cases the FCW contained the main fraction, 53-84%, of the CTO. In contrast the proportion of dissolved solids in the FCW was nearly constant, 42-47%. From the data for the CTO and the dissolved solids in the FCW one may deduce that the chips retain the CTO somewhat preferentially over the cooking liquor. Furthermore, industrial practice generally combines digester liquor from the blown digester charge with brown stock washings and subsequently raises the concentration of solids in the combined liquors to 25-30% by multiple evaporators. Tall oil soaps form readily on the surface of the partially concentrated black liquor and are removed by skimming as a first step in tall oil recovery. Thus, much of the CTO from the FCW, as listed in Table IX, would be recovered as tall oil in commercial practice.

TABLE IX

LABORATORY KRAFT COOKS OF LOBLOLLY PINE CHIPS. SECOND SERIES

(see Table IV for process data and cooking schedule)

Digester Description	A Control, (unextracted) chips	B Benzene-ethanol-Extracted Chips	C Acetone-extracted Chips	D Unextracted Chips + 1.5% Fatty Acids	E Unextracted Chips + 1.5% Resin Acids	F Acetone-extracted Chips + 2% Fatty Acids	G Acetone-extracted Chips + 2% Resin Acids
Yield of pulp, % o.d. wood	45.6	49.4	48.8	46.8	47.1	49.1	50.5
Kappa number	35.7	35.1	38.3	52.4	52.0	49.6	52.0
Solids content of black liquor, % by weight	17.4	18.2	17.1	17.1	17.6	17.5	17.9
Crude tall oil (CTO) extracted from lower fraction of black liquor, % solids	0.90	0.31	0.29	0.68	1.13	0.41	1.18
CTO solubility, g/100 g black liquor	0.157	0.055[c]	0.050[c]	0.116	0.199	0.072	0.211
CTO in skimmable soap, % o.d. wood	0.22	--[b]	--[b]	0.45	0.48	0.16	0.16
CTO in fiberized chip washings (FWC) % o.d. wood[a]	1.13(65)	0.23(64)	0.18(58)	1.87(72)	1.50(60)	1.82(84)	0.78(53)
CTO dissolved in black liquor, % o.d. wood	0.38	0.13	0.13	0.29	0.50	0.19	0.54
CTO, totals, % o.d. wood	1.73	0.36	0.31	2.61	2.48	2.17	1.48
Dissolved solids in FCW, % of total dissolved solids (TDS)	47	47	42	43	43	43	42

[a] The numbers in parentheses are percentages of the total CTO isolated from the FCW.
[b] No soap scum formed on these liquors.
[c] This concentration is less than the solubility.

In order to close up the procedures for a complete summative analysis and to improve the efficiency of CTO recovery, future experiments will include analysis of the final pulp (8) in addition to the liquors.

By inspection of the data for the solubility of CTO in black liquor, Table IX, the addition of fatty acid salts appeared to lower the solubility of CTO, and resin acid salts to raise the solubility of the CTO in the liquor. However, the picture was complicated by the fact that added fatty acid salts appeared to penetrate the chips somewhat more readily than the sodium resinates. Even so, the solubility of the CTO in the liquor from the control (Table IX, column Ⓐ) was intermediate between that of chips spiked with fatty acids (columns Ⓓ and Ⓕ) and chips spiked with resin acids (columns Ⓔ and Ⓖ). Additional experiments will be attempted to explore further the influence of resin acids on the solubility of CTO in black liquor.

Fractionation of CTO and Analysis by Gas Chromatography (GLC).
Second Series

The method of Zinkel (6,7) was used to fractionate CTO into neutrals (unsaponifiables), fatty acids, and resin acids. CTO from all cooks except those with unextracted chips produced the results summarized in Table X. All fractionations were about as expected based on the history of each cook.

The analysis of the acid fractions by GLC produced the results summarized in Table XI. Only the CTO obtained from the upper fractions of black liquor and from fiberized chip washings (FCW) were analyzed. The chromatograms were typical in most respects when compared with the results generally obtained in the analysis of CTO. However, the abietic/dehydroabietic acid ratios showed marked differences between the upper fraction and the FCW from the same cook. No direct explanation is available at present, but the ratios of abietic/dehydroabietic acid are similar

to those observed in oxygen-alkali pulping (9). One possible explanation may reside in the fact that cooked chips, saturated with the alkaline black liquor, were fiberized in a Waring Blendor with hot water. The violent action of the blender which favors the intimate contact between the air in the blender and the alkaline solution of residual black liquor may result in the rearrangement-oxidation of abietate to dehydroabietate. Experiments are being planned to determine whether or not such treatment can account for these observations.

TABLE X

FRACTIONATION OF CTO FROM LABORATORY KRAFT COOKS OF LOBLOLLY PINE. SECOND SERIES

Black Liquor Sample No. and Description of Experiment	CTO Basis o.d. wood, %	Fractions as % CTO		
		Neutrals (Unsap.)	Fatty Acids (as methyl esters)	Resin Acids
(A) Control, unextracted chips				
Upper fraction	0.43	12.4	48.4	36.2
FCW[a]	1.13	n.a.[b]	n.a.	n.a.
(D) Unextracted chips + 1.5% fatty acids				
Upper fraction	0.57	8.8	65.4	21.1
FCW	1.87	8.0	63.4	28.6
(E) Unextracted chips + 1.5% resin acids				
Upper fraction	0.68	10.3	38.0	43.5
FCW	1.50	8.6	46.9	44.5
(F) Acetone-extracted chips + 2% fatty acids				
Upper fraction	0.25	8.2	83.1	4.6
FCW	1.82	10.7	86.9	2.4
(G) Acetone-extracted chips + 2% resin acids				
Upper fraction	0.37	10.1	18.1	67.2
FCW	0.78	12.7	29.7	57.6

[a] FCW = Fiberized chip washings.
[b] n.a. = Not analyzed.

TABLE XI

GLC ANALYSIS OF TALL OIL FATTY ACIDS AND RESIN ACIDS AS METHYL ESTERS
FROM LABORATORY KRAFT COOKS OF LOBLOLLY PINE

Fatty Acid Derivatives[a]	Retention Time, min	Composition Based on Fraction Analyzed, %								
		A	D		E		F		G	
		Control, upper fract.	Unextracted Chips + 1.5% F.A.		Unextracted Chips + 1.5% R.A.		Extracted Chips + 2% F.A.		Extracted Chips + 2% R.A.	
			Upper Fract.	Fiberized Chip Wash	Upper Fract.	Fiberized Chip Wash	Upper Fract.	Fiberized Chip Wash	Upper Fract.	Fiberized Chip Wash
C_{16}	--	1.8	<1	<1	1.8	2.0	<1	<1	8.8	14.8
Palmitic	4.6-4.7	8.3	4.9	5.9	8.8	9.5	2.9	3.1	11.1	13.0
Palmitoleic	5.5-5.7	2.4	1.6	2.0	2.6	3.0	1.1	1.3	3.9	5.1
C_{17}	6.2	<1	<1	<1	<1	<1	<1	<1	<1	1.2
Unknown	7.4-7.6	<1	<1	<1	<1	<1	<1	<1	<1	1.9
Stearic	8.3-8.4	3.2	2.4	3.4	3.0	4.1	2.4	2.8	4.8	7.8
Oleic	9.8-9.9	37.2	46.4	49.0	40.8	43.2	46.1	53.9	26.9	27.4
C_{19}	11.1-11.2	1.3	0.9	1.1	1.0	1.1	<1	<1	1.2	1.5
Linoleic	12.5-12.7	20.2	26.7	26.3	22.8	22.6	28.6	29.4	10.5	9.4
C_{20}	14.3-14.8	2.6	1.9	1.7	2.1	2.4	1.9	1.4	3.8	2.8
Linolenic	17.3-17.5	6.9	4.7	5.0	4.9	4.3	5.0	4.8	8.7	5.3
Unknown	19.3-19.5	1.7	0.8	<1	1.3	1.4	--	--	2.7	--
Unknown	20.5	5.5	4.6	1.5	3.2	1.4	7.1	2.0	8.1	3.7
Unknown	22.3-22.5	3.5	1.5	<1	2.1	1.4	1.8	<1	4.2	2.1
C_{22}	25.1-25.4	3.9	1.6	1.2	3.2	3.0	1.2	--	2.8	1.5
C_{22}	26.5-26.8	1.4	0.6	<1	1.5	<1	--	--	4.5	3.9
Resin Acid Derivatives[a]										
(Fatty acids)	0.0-12.0		1.3	6.3	0.9	4.7	30.9	50.3	<1	3.6
Unknown	13.0-13.3		0.4	<1	0.3	<1	14.4	13.0	<1	--
Tetrahydroabietic	14.1-14.4		0.8	1.1	1.0	<1	13.4	14.2	1.5	2.1
Pimaric	16.1-16.4		11.3	13.9	7.8	11.0	14.8	27.6	4.0	6.3
Sandaracopimaric	18.0-18.2		1.5	2.6	2.1	2.9	3.5	3.0	2.2	4.4
Dihydroabietic	20.1-20.5		<1	<1	<1	<1	3.4	7.9	<1	1.0
Palustric + Levopimaric	22.0-22.2		1.4	--	2.6	<1	--	--	2.8	--
Isopimaric	23.4-23.7		2.8	4.0	8.2	12.7	3.9	3.3	15.6	27.6
Unknown	28.1-28.3		0.6	--	2.0	--	--	--	<1	--
Abietic	34.2-34.7		37.2	2.6	45.9	3.2	8.8	<1	50.7	0.9
Dehydroabietic	37.9-38.7		43.8	72.7	27.4	60.0	31.3	52.0	18.4	52.9
Neoabietic	44.7-45.0		0.2	1.9	<1	2.0	1.4	2.5	<1	4.7
Unknown	40.5-40.7		--	--	1.2	--	--	--	1.1	--

[a] As methyl ester.

SUMMARY AND CONCLUSIONS

Five kraft mills furnished both to-the-skimmer liquors and from-the-skimmer liquors which were analyzed for extractable crude tall oil (CTO) and ranged from 1.24 to 2.13% to-the-skimmer and 0.39 to 0.78% from-the-skimmer, based on o.d. liquor solids. Fractionation of the CTO and analysis of the acids by gas chromatography were within the normal ranges for commercial tall oils.

The analysis of aliquots of black liquors stored at room temperature in air-tight, polyethylene bottles showed no significant loss of CTO upon storage for approximately one year.

In one experiment, air was bubbled through the black liquor but no loss of CTO due to air-oxidation was observed.

Two series of laboratory-scale kraft cooks were performed with loblolly pine chips; one cook with aspen chips was included in the series. The black liquors were drained from the cooked chips and, after standing overnight, were analyzed for CTO in an upper fraction which included the soap scum, and a lower fraction. The results from the first series produced approximately half the CTO known to be present in the cooks. In the second series, the washings from the mechanical fiberizing of the chips were included in the analyses and resulted in nearly quantitative recovery of CTO. The distribution of CTO between the decanted black liquor and the fiberized chip washings indicated that CTO salts are held preferentially by the cooked chips over the cooking liquor. Analyses by gas chromatography of the CTO indicated that manipulations which expose the resin acid salts to high concentrations of air (oxygen) may be responsible for the marked conversion of abietic to dehydroabietic acid in such cases.

FUTURE WORK

1. It was observed that the presence of resin acids in amounts greater than the fatty acids tended to increase the solubility of CTO in the black liquor. One experiment will consist of adding controlled amounts of each, fatty and resin acids, to an excess of sodium hydroxide with a subsequent measurement of the amount and composition of dissolved CTO. A companion series will be performed with the substitution of skimmed black liquor for the sodium hydroxide. These experiments should yield data about the solubility of tall oil soaps in black liquor.

2. Experiments are planned to test the behavior of resin acids in alkaline solution in a Waring Blendor. The exposure to (a) nitrogen, (b) air and (c) oxygen should yield information about the effect of violent mechanical action in the presence of air, such as in the fiberizing of chips, on the abietic acid/dehydroabietic acid ratio.

3. The use of lightered (resin-soaked) wood (Paraquat-treated slash pine, now on hand) is planned to study the effect of enriched or exaggerated amounts of resin acids on the recovery of CTO in kraft pulping.

EXPERIMENTAL

Black Liquors

Samples of "to-the-skimmer" and "from-the-skimmer" black liquors were obtained from five pulp mills, identified in Table I. In general, "to-the-skimmer" liquors were received in five-gallon pails and "from-the-skimmer" liquors in 50-gallon drums. Since reconstitution of the liquors (redissolving of the precipitated soap scums) was impossible, the contents of each sample were mixed thoroughly and ten representative, one-pint aliquots were placed in PE bottles. Some of the

bottles were stored in a refrigerator and some at room temperature. Subsequent analyses utilized the entire contents of one bottle per analysis in order to account for all the tall oil present.

After the aliquots for analyses were removed, the stirrer was removed and the soaps were allowed to reform a scum on the surface of the liquor. After standing for a few hours (or overnight) the soaps were skimmed by hand and reserved for analysis. However, because of mechanical losses, the yields of tall oil could not be determined accurately from such skimmings.

Pulpwood Samples

Loblolly Pine

Bolts of loblolly pinewood were supplied by Champion International in Canton, North Carolina. This is the same wood that is being used in the concurrent Funded Formal Projects 3264 and 3266 on oxidative pulping and fate of tall oil components, respectively.

Trembling Aspen

Trembling aspen logs were supplied by Wausau Paper Mills Company from their forest in the vicinity of Rhinelander, Wisconsin.

Slash Pine

Bolts of normal and Paraquat-treated slash pine were supplied by Mr. William Peters of the U.S. Forest Service from trees cut in the Owens-Illinois, Inc. forest near Olustee, Florida.

Production of Chips for Pulping

The loblolly pinewood and the aspenwood were chipped in a mechanical chipper to produce commercial type chips. The slash pinewood was cut into disks

which were chipped by hand with a hinged knife. In the case of the Paraquat-treated slash pinewood, the resin-soaked portions were separated from the disks before chipping.

Pulping Equipment and Conditions

All pulping was done in stainless steel cylindrical digesters 53 mm in inside diameter by 240 mm in height and 3.5 mm wall thickness, and 530 ml volume. Each digester was closed by a two-piece threaded cap sealed with a teflon ring gasket. As many as seven such units can be mounted in a rotating rack and immersed in an electrically heated oil bath. Four of the units are equipped with valves for degassing and for pressurizing with gases. The cooking conditions for the kraft experiments are listed in Table VI.

Analytical Procedures

Determination of Total Solids

Two 10 ml aliquots of black liquor were weighed, then taken to dryness in tared evaporating dishes at 105° for approximately 4 hours, cooled in a vacuum desiccator, and reweighed.

Extraction of Crude Tall Oil (CTO)

The liquor sample (contents of one 500 ml bottle) was transferred quantitatively to a large beaker, diluted with distilled water to a volume approximately 5-6 times the original volume and a specific gravity of 1.024 to 1.030, or about 5% solids. A total solids content on the dilute liquor was determined as described previously.

Extraction of the tall oil as detailed by Saltsman and Kuiken (2) was applied with the following exceptions: (a) after each addition of petroleum ether (35-65°), the solution was shaken by hand for 5 minutes; (b) the petroleum ether extract, filtered and dried over anhydrous sodium sulfate, was evaporated to dryness

on a rotary vacuum evaporator; (c) initial losses incurred by vacuum filtration of the tall oil through a fine porosity sintered glass funnel were avoided in future samples by filtering under gravity through cotton into a tared round-bottomed flask; and (d) to minimize color degradation and air oxidation of the tall oil residues, samples were dried at 105°C for less than 5 minutes, flushed with nitrogen, and cooled in a vacuum desiccator in the presence of potassium hydroxide pellets.

Analysis of Soap Skimmings

Precipitated soaps were collected by skimming the remaining black liquor sample, both to and from the skimmers after a retention time of several hours (or overnight) following prior removal of the liquor samples.

Aliquots of soap were dried at 105°C to determine total solids. Soap samples of 1 to 3 g were transferred to a 1,000 ml separatory funnel and dissolved in 100 ml of distilled water, 5 g or less of anhydrous sodium sulfate was shaken with the skimmings until dissolved, followed by the addition of 10 ml of HCl solution (1:1 v/v $HCl:H_2O$) to a pH of 2. The aqueous layer was then extracted in the same manner as for kraft black liquor (2). Tall oil content of the soap was calculated both on a dry-weight soap solids basis and the wet-weight, as shown in Table III. In addition to the method described, two additional quantitative procedures for determining tall oil content in soap are detailed by Browning (3).

Analysis of Tall Oil

Chemical Separation of Neutral and Acidic Materials — Assuming the conditions of the kraft process were rigorous enough to saponify the neutrals, separation of the unsaponifiables was effected by an alkaline extraction of an ether solution as described by Browning, Buchanan, et al. (3-5).

Separation of the fatty and resin acids was accomplished by selective esterification in 20 ml methanol catalyzed by 1 ml methyl sulfuric acid. The mixture was refluxed gently for 30 minutes.

For essentially quantitative separation of the fatty acid methyl esters and the free resin acids, a modification of the method developed by Buchanan was used (4). Following esterification, the mixture was allowed to cool to 25°C, and the amount of methanol, plus water, was adjusted to less than half the volume of ether added, to assure layer separation. The mixture was extracted twice with 25-ml portions of 1% sodium hydroxide. The combined ether extracts were extracted once more with 25 ml of 1% sodium hydroxide and washed twice with 10 ml portions of water, transferring the washings and sodium hydroxide extracts to the aqueous solution. The ether extracts were washed with additional 10 ml portions of water until neutral to phenolphthalein, dried over anhydrous sodium sulfate and evaporated to give the fatty acid methyl esters.

To ensure quantitative recovery of the resin acids, the acidified aqueous solution was extracted four times with 30 ml portions of ether. The ether extracts were washed with two 10-ml portions of water, dried over anhydrous sodium sulfate, and evaporated and dried to constant weight. The resin acids, dissolved in 5 ml ether-methanol (9:1, v/v), were methylated with freshly prepared diazomethane. Excess diazomethane, added to ensure complete esterification, was removed by vacuum evaporation.

In later work, all samples were subjected to nitrogen purge after drying, and 1% solutions were prepared in chloroform, blanketed with nitrogen and sealed in Reacti-Vials[1] for refrigeration prior to GLC analysis.

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[1]Trade mark for screw-capped vial with rubber diaphragm, available from Pierce, P.O. Box 117, Rockford, Illinois 61105.

Separations on a Column of DEAE-Sephadex[1] — The quantitative separation of CTO into neutral and acidic materials was accomplished by the use of an ion-exchange material, DEAE-Sephadex, and a mixed organic solvent according to the general procedure of Zinkel and Rowe (6,7). Experience in our laboratory demonstrated that a period of ≥ 48 hours for the conditioning of the DEAE-Sephadex in the operating solvent (ethyl ether-methanol, 9:1, v/v) was essential for the optimum efficiency of separation[2]. The DEAE-Sephadex, 4 g, was packed in a water-jacketed tube (1.0 cm ID x 8-10 cm in length). The capacity of the column was approximately 1 meq (<300 mg of fatty and resin acids). In operation the tall oil was dissolved in 5 ml of ethyl ether-methanol-water (89:10:1, v/v) and placed on the column, the neutrals were washed through with 50-100 ml of the same solvent, and the acids were then removed with 250 ml of carbon dioxide-saturated ethyl ether-methanol, 9:1.

Purification of Methyl Esters with Alumina

Methyl esters of fatty and resin acids were dissolved in benzene and the solutions were percolated through a column of alumina (Woelm, neutral, activity I)[3] and washed with 10-12 volumes of benzene.

Analysis of Tall Oil Fractions by Gas Chromtography

Benzene (or chloroform) solutions (1%) of the methyl esters of fatty and resin acids were injected onto a column (6 ft x 1/8 inch, stainless steel) packed with 10% EGSS-X, at a temperature of 180°C for fatty acid esters and 200°C for resin acid esters. A hydrogen flame ionization detector was used with helium carrier gas in the column at 25 ml per minute.

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[1]DEAE-Sephadex, A-25, was obtained from Pharmacia Fine Chemicals, Inc., 800 Centennial Avenue, Piscataway, New Jersey, 08854.
[2]Attempts were made to regenerate used DEAE-Sephadex but the results were unsatisfactory.
[3]Purchased from ICN Pharmaceuticals, Inc., 26201 Miles Road, Cleveland, Ohio, 44128.

Individual components were identified presumptively by relative retention times and by comparison with authentic references.

Simulated Skimming of Tall Oil Soaps

At the end of each cook, the reactor was cooled to 80-90°C and opened, and the hot liquor was decanted from the chips through a 150 mesh, stainless steel screen into a beaker. After standing undisturbed overnight at room temperature, the lower 40-60% of the liquor was removed by a siphon to another vessel and both portions were analyzed for extractable tall oil. The amount of tall oil in the upper portion, corrected for dissolved tall oil, was defined as skimmable tall oil soap. The method is similar to that reported by Bolger and Hopfenberg (1).

Exposure of Concentrated Kraft Black Liquor (to Skimmer) to Air

Approximately 500 ml of concentrated kraft black liquor (to skimmer) was placed in a glass cylinder and a stream of air was bubbled through the liquor at 15-minute intervals over a period of three hours. The liquor was allowed to stand exposed to the air over a week-end and again air was bubbled through the liquor at intervals over a three-hour period. It was necessary to interrupt the stream of air to avoid losses of liquor and soaps due to foaming. The entire sample was diluted with water and analyzed for extractable tall oil in the usual way; yield of tall oil, 1.58% on basis of o.d. solids. The tall oil was fractionated into neutrals, 14.4%; fatty acids (as methyl esters), 44.3%; resin acids, 43.6%, based on the crude tall oil.

ACKNOWLEDGMENTS

We gratefully acknowledge the work of staff members Mrs. Bruce Alward and Mr. John Peckham without whose assistance this work could not have been done.

CHAPTER II

PRELIMINARY EXPERIMENTS ON THE SEPARATION OF TALL OIL COMPONENTS BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

The present report records our experience on the use of our high performance liquid chromatographic equipment for the separation, detection, and measurement of the components of tall oil. Our equipment comprised the following individual items:

1. Varian Model 8500 liquid chromatograph complete with stop flow injector, two pumps, and solvent mixer.
2. Perkin-Elmer Model LC-55 continuously variable-wavelength spectrophotometric detector.
3. Varian Model A-25 dual pen recorder with Disc integrator.
4. Assorted columns.

Two standard tall oil component solutions were prepared in acetonitrile as follows:

A. Loblolly pinewood extractives were saponified, and the crude tall oil was isolated from the saponification mixture by the method of Saltsman and Kuiken (2). The mixed fatty and resin acids were separated from the neutrals by the method of Zinkel (7) and dissolved in acetonitrile to give a solution containing 1.19×10^{-2} mg/microliter.

B. The tall oil from a kraft cook of fatty acid-spiked loblolly pinewood chips was isolated by the Saltsman and Kuiken procedure and separated into neutral and combined acid fractions by the Zinkel method. The combined acids were dissolved in acetonitrile to give a standard solution containing 1.3×10^{-3} mg/microliter.

PRELIMINARY EXPERIMENTS

In a demonstration experiment by the Perkin-Elmer product engineer the components of aspen leaf extract were easily separated on Perkin Elmer's reverse phase Octadecyl Sil-X-I (Sil-X-I-C_{18}) column using mixtures of acetonitrile in water as eluting solvents and detection at 195 nm wavelength. Accordingly, our first experiments were performed on a 4.6 mm ID and 50 cm long Sil-X-I-C_{18} column with acetonitrile-water mixtures at 195 nm. We found that gradient elution gave no better separation of components than did isocratic elution with 60% acetonitrile in water, and gradient elution gave a changing base line due to change in the absorption of the solvent mixture with concentration change. Even though we obtained considerable separation of tall oil components under these conditions, we believed that we were missing important components in our systems because of absence of absorption at the 195 nm wavelength. Furthermore, because of the dependence of detector response on the specific absorption of the component at 195 nm, it was obvious that the appearance of the chart record did not give a true picture of the composition of our mixtures.

EFFECT OF WAVELENGTH OF DETECTION ON CHROMATOGRAMS

To test the effect of wavelength of detection on the nature and amount of individual components as indicated by the chart record, a series of runs was made with the Sil-X-I-C_{18} column isocratically at 60% acetonitrile in water changing the wavelength of detection from 193 nm to 254 nm. The following operation parameters were maintained constant:

Flow rate:	60 ml/hr
Injection:	5 microliters standard tall oil Solution A
Chart span:	10 mv
Chart speed:	0.25 in/min

The chromatograms obtained are pictured in Fig. 1-3. The curves of Fig. 1-3 demonstrate that the sensitivity of components toward detection varies tremendously with wavelength. The chromatogram at 193 nm (Fig. 1a) bears little resemblance to that at 254 nm (Fig. 3b). The 220 nm curve (Fig. 2c) appears to be out of place by the location of its maxima, but a repeat chromatogram gave identical results.

The 5 microliter injection of standard tall oil solution A contains 0.0595 mg of acids from saponified loblolly pinewood extractives. With the recorder span of 10 mv and with a detection wavelength of 193 nm (Fig. 1a), the major peak at 12.5 minutes was 1.73 times the chart scale. Other major peaks occurred at 9.6 minutes (0.36 scale), 18.3 minutes (0.77 scale), and 24.0 minutes (0.33 scale).

As the wavelength of detection increased, the nature and location of the peaks changed in addition to the sensitivity of detection. The major peak at 12.5 minutes remained the major peak in the chromatograms until 230 nm (Fig. 2d), when the major peak occurred at 17 minutes. The actual location of the major peak gradually moved until at 254 nm, it occurred at 15.5 minutes. During the changes in wavelength from Fig. 1a to Fig. 3b, most of the original peaks had disappeared, and new ones appeared.

Thus, we know that a great many components are present in this acid fraction of the saponified pinewood extract, and our present detection system is inadequate for the detection of all of them at one time. For the evaluation of tall oil mixtures of this type it is obvious that a universal type of detector (such as the moving wire type) is required.

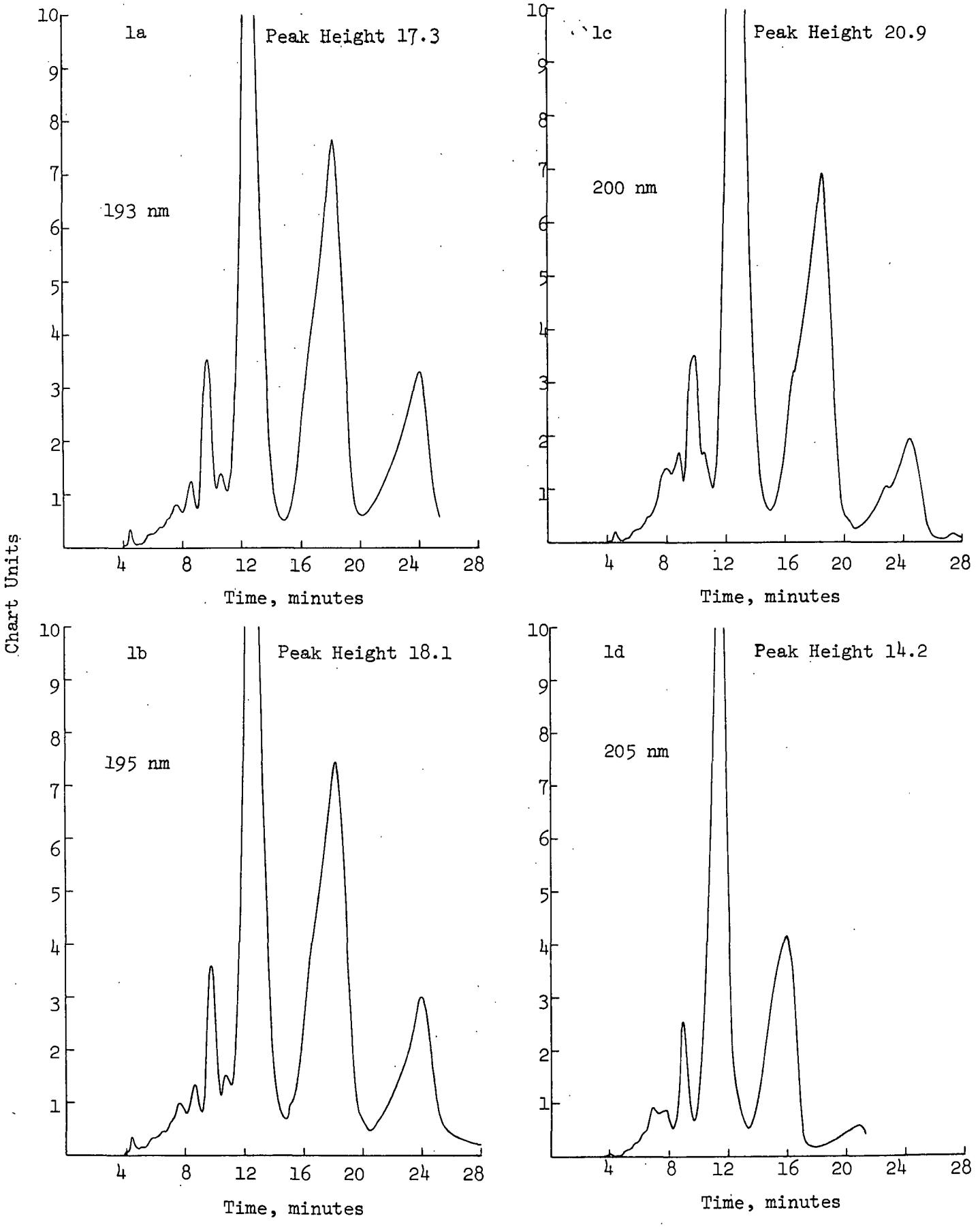

Figure 1. Liquid Chromatograms on Sil-X-I-C_{18} with 60% Aqueous Acetonitrile of 5 Microliters Tall Oil Standard A at 60 ml/hr, 10 mv Chart Span, and Varying Wavelength Detection

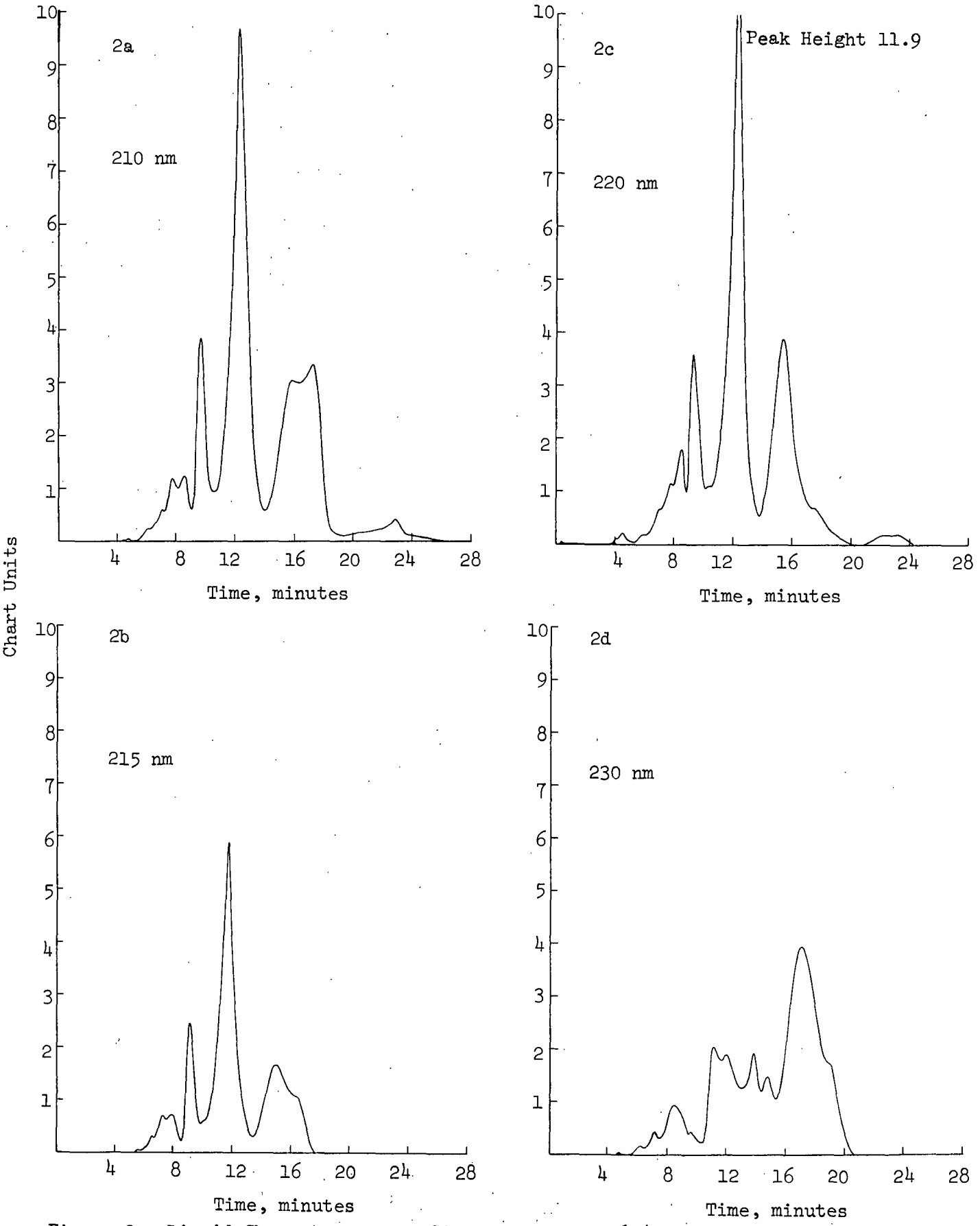

Figure 2. Liquid Chromatograms on Sil-X-I-C_{18} with 60% Aqueous Acetonitrile of 5 Microliters Tall Oil Standard A at 60 ml/hr, 10 mv Chart Span, and Varying Wavelength Detection

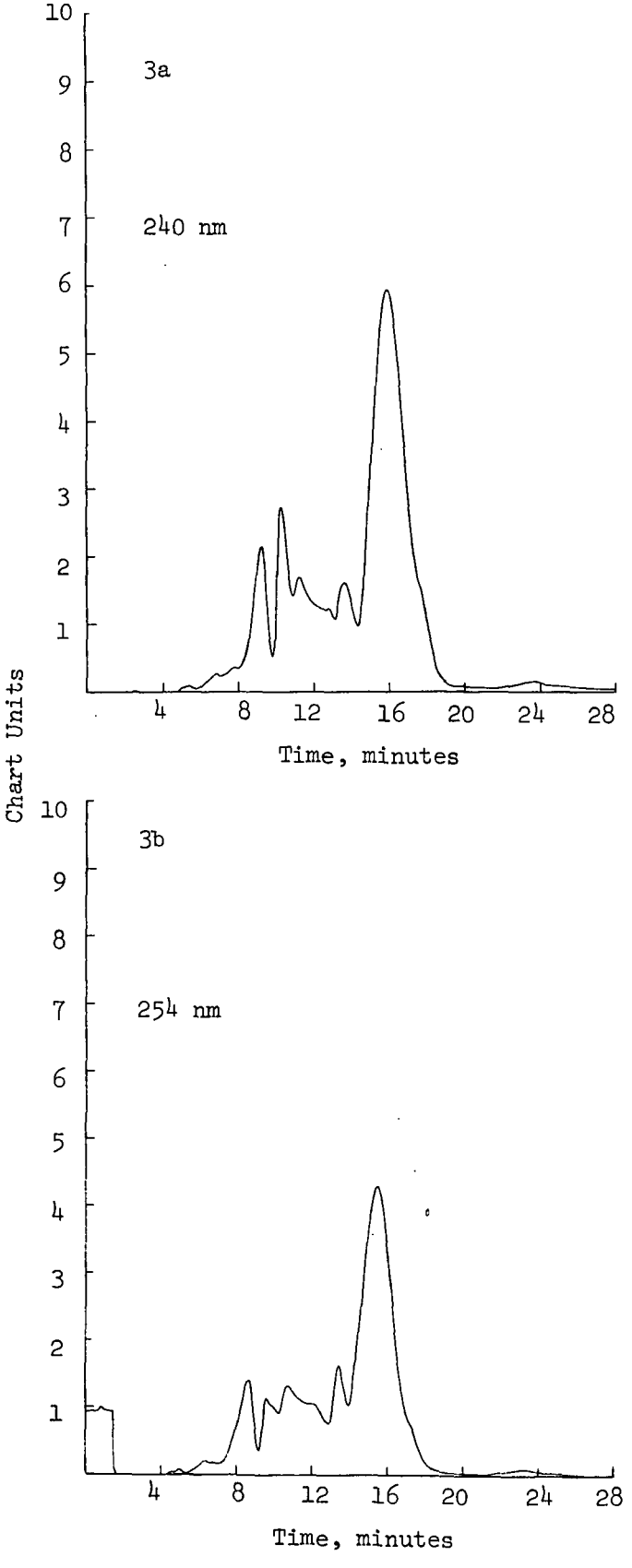

Figure 3. Liquid Chromatograms on Sil-X-I-C_{18} with 60% Aqueous Acetonitrile of 5 Microliters Tall Oil Standard A at 60 ml/hr, 10 mv Chart Span, and Varying Wavelength Detection

For future studies on the high performance liquid chromatography of tall oil fractions with our equipment a detection wavelength of 200 nm was selected arbitrarily, because this wavelength appeared to give us a good compromise of resolution and sensitivity.

EXPERIMENTS WITH SAMPLE SIZE AND CHART SPAN

In working with tall oil mixtures it soon became apparent that at the 200 nm wavelength some components gave tremendous detector response compared with others. It was also found that the 5-microliter sample size for tall oil standard solution A was much too large, and that 3-microliter and 2-microliter samples were adequate for good chromatograms. For better looking chromatograms, the chart span could be varied to accommodate the large detector response of some peaks and the lesser response of others. Thus Fig. 4 is a chromatogram of 2 microliters of tall oil standard solution A at 200 nm with an initial chart span of 10 millivolts, a span of 20 millivolts at 8 minutes, and a span of 10 millivolts at 16 minutes. Figure 4 differs somewhat from Fig. 1c because the column was eluted with 65% acetonitrile in this case, whereas 60% acetonitrile was employed in the earlier experiment.

EXPERIMENTS WITH WATERS' μBONDAPAK C-18 COLUMN

At the suggestion of Varian's product engineer, we obtained a μBONDAPAK C-18 column from Waters Associates. This column was reputed to be the most effective of the reverse phase columns available for high performance liquid chromatography. The column was 4 mm ID by 30 cm in length.

A series of isocratic elutions was made with the detector wavelength set at 200 nm, a recorder span of 10 mv, and a flow rate of 60 ml per hour. A

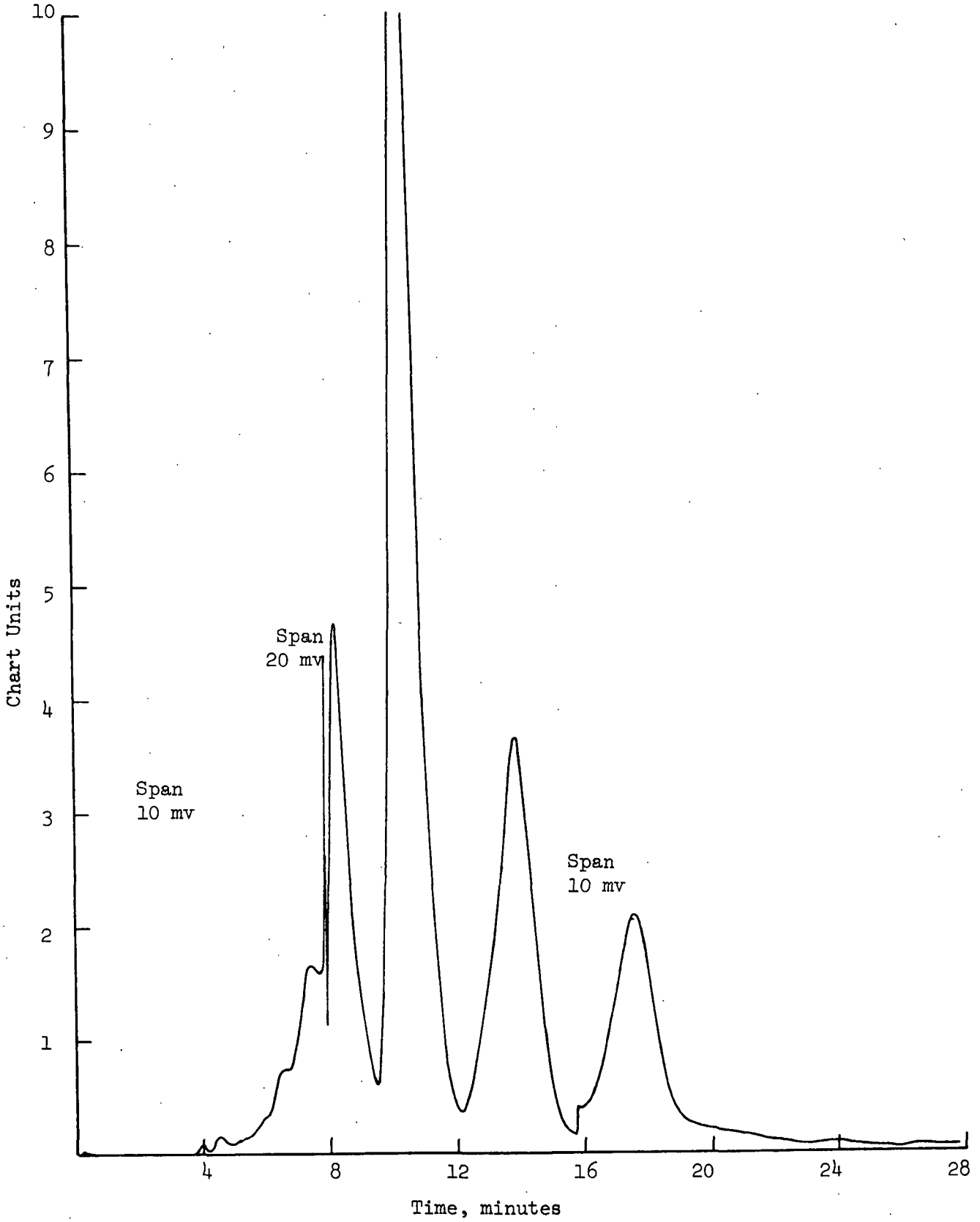

Figure 4. Liquid Chromatogram on Sil-X-I-C_{18} with 65% Aqueous Acetonitrile of 2 Microliters Tall Oil Standard A at 60 ml/hr, 200 nm Detection, and Varying Chart Span

3-microliter injection of tall oil standard solution A with isocratic elution with 65% acetonitrile in water gave six major peaks with the main peak at 6.5 minutes going off chart scale. All major peaks had minor peaks and shoulders. The pressure was 800 psig. Isocractic elution with 60% acetonitrile gave essentially the same chromatogram, but this time the major peak was just 1.13 times chart scale (see Fig. 5).

Isocratic elution with 55% acetonitrile spread out the earlier peaks presumably due to fatty acids, but the major peak, presumably resin acids, came off at 14.5 minutes. Dropping the concentration of acetonitrile to 50% gave good resolution of the early peaks, a break of 6 minutes when the base line of the chart was below zero, and then the main peak at 16 minutes (see Fig. 6). As the concentration of acetonitrile was lowered, the resolution of the resin acid peaks became poorer, but the resolution of the fatty acids became better. Accordingly, experiments with gradient elution were tried in an attempt to separate the fatty acids at low acetonitrile concentration, and then get good resolution of the individual resin acids as the acetonitrile concentration increased.

A number of gradients were tried. Figure 7 represents a gradient starting at 40% acetonitrile and increasing to 85% acetonitrile at the rate of 2% per minute. After reaching 85%, the concentration of acetonitrile was maintained. It should be noted that resolution of peaks has increased, and more individual peaks are now in evidence.

More trials of gradients were made. During these trials it was noted that many times the detector would go negative indicating a solution with less absorbance than the solvent and suggesting the presence of fluorescent material at the 200 nm wavelength. In order to keep a record of this negative absorption,

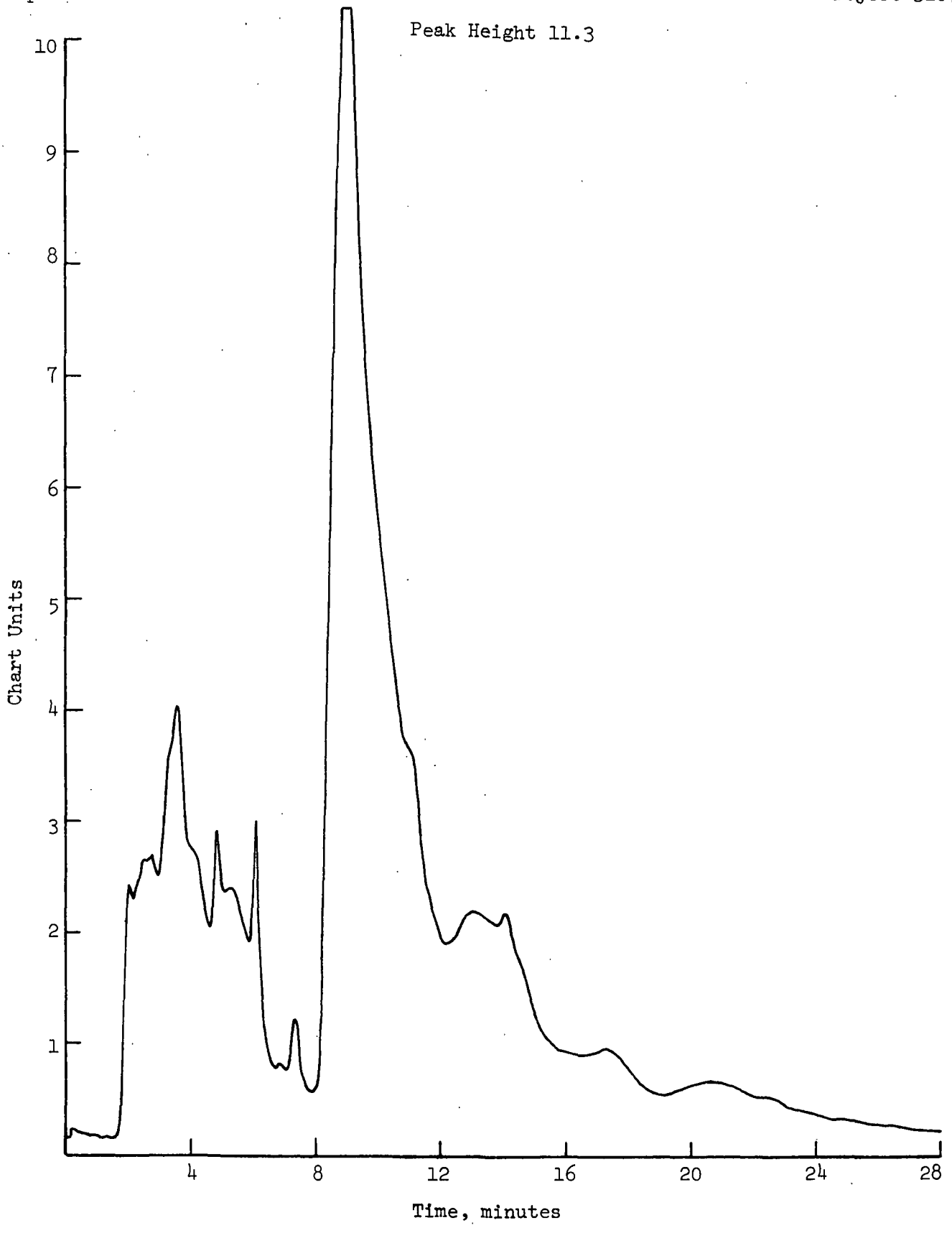

Figure 5. Liquid Chromatogram on μBONDAPAK C-18 with 60% Aqueous Acetonitrile of 2 Microliters Tall Oil Standard A at 60 ml/hr, 200 nm Detection, and 10 mv Chart Span

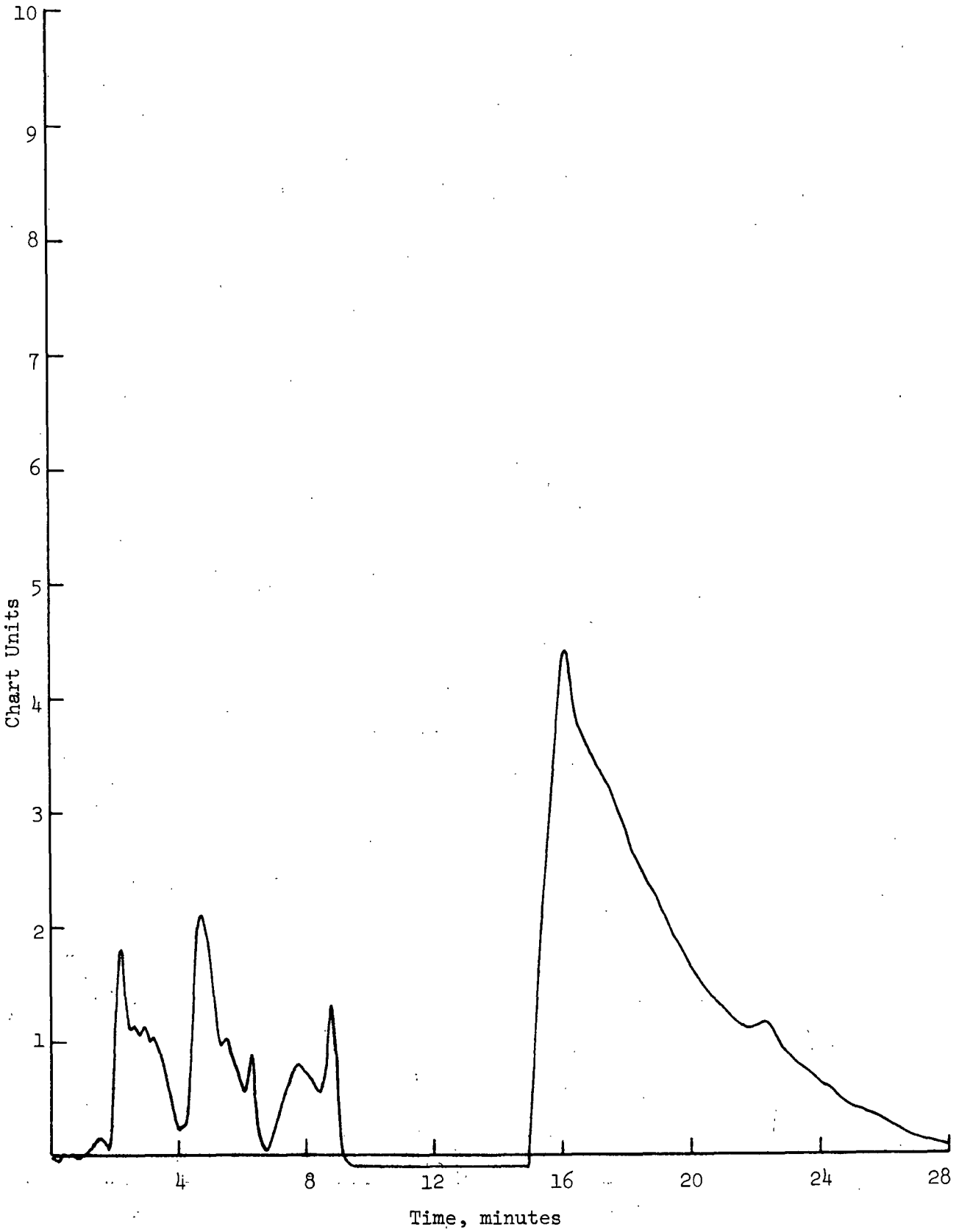

Figure 6. Liquid Chromatogram on μBONDAPAK C-18 with 50% Aqueous Acetonitrile of 2 Microliters Tall Oil Standard A at 60 ml/hr, 200 nm Detection, and 10 mv Chart Span

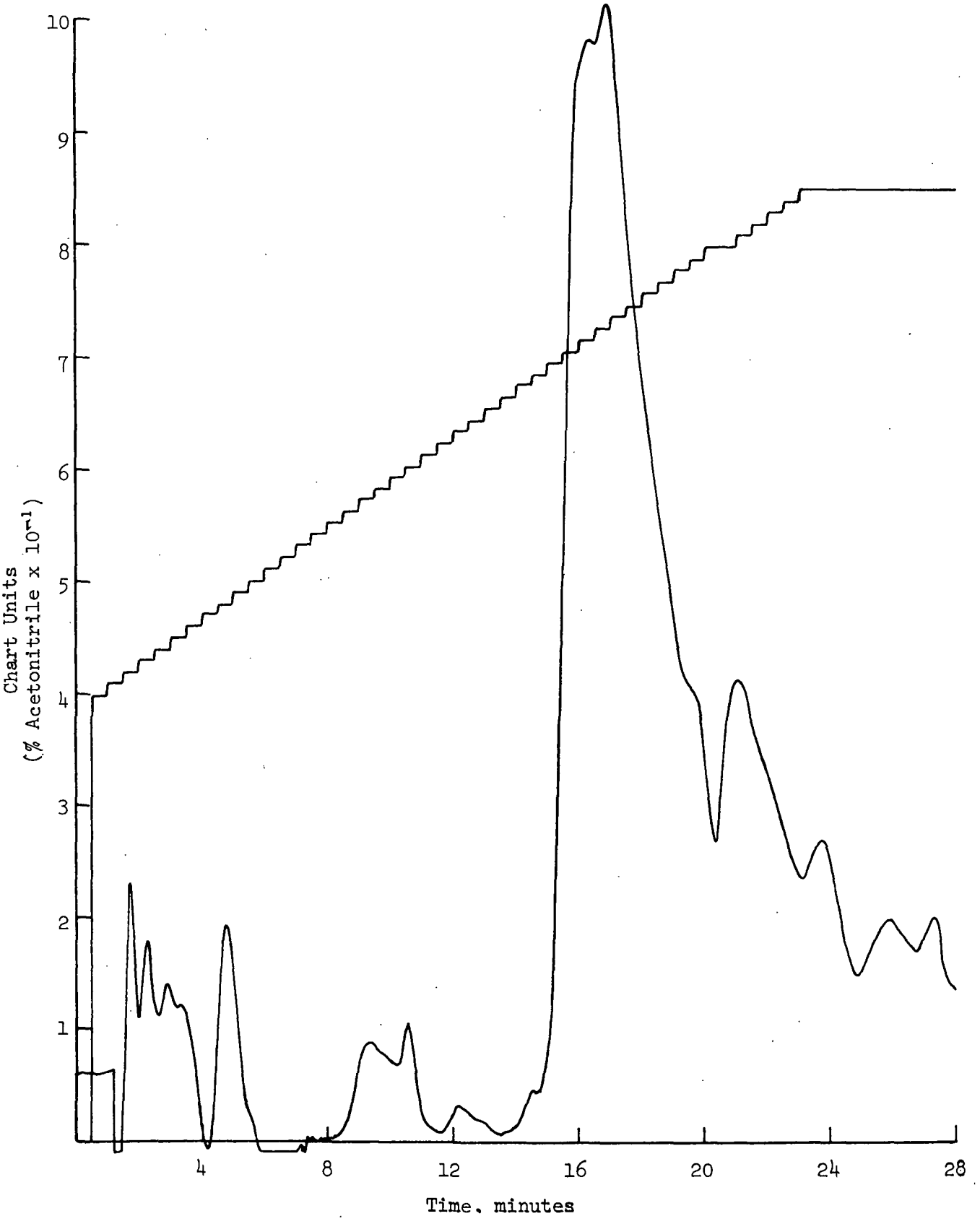

Figure 7. Gradient Elution Liquid Chromatogram on μBONDAPAK C-18 with Aqueous Acetonitrile of 2 Microliters Tall Oil Standard A at 60 ml/hr, 200 nm Detection and 10 mv Chart Span

the zero line for the chromatogams was set arbitrarily at 10 chart units. Even under these conditions, the absorption sometimes went negative.

Gradients were run from 40% acetonitrile to 100% acetonitrile varying the slopes of the gradients at different portions of the chromatogram. During these gradient runs ending at 100% acetonitrile, when the concentration was suddenly dropped to 40% for the next chromatogram, it was noted that some material came off the column in fairly sharp bands. Therefore, a negative gradient was applied at the end of the chromatogram in order to record this material. Ultimately, a gradient was evolved which resolved as many as 18 individual sharp peaks along with some broad peaks. Such a gradient is pictured in Fig. 8 which indicates much better resolution of individual components than the isocractic elution of Fig. 5. Unfortunately, the good resolution has been at the expense of time. [Note the different time scale in Fig. 8.] In the chromatogram of Fig. 8 the acetonitrile concentration was raised from 40 to 53% at the rate of 1% per minute, maintained at 53% for 13 minutes, raised to 95% at the rate of 2% per minute, decreased to 40% at the rate of 10% per minute, and maintained at 40% until finished. It should be noted that the absorbance base line goes up as the acetonitrile concentration increases.

A number of our authentic fatty acids and resin acids were subjected to this same gradient in order to identify individual peaks of the chromatogram of Fig. 8. The first peak at 4 minutes was identified as oleic acid, and the largest peak on the chromatogram at 25.5 minutes was identified as dehydroabietic acid. All of our other authentic compounds were found to be very crude, and because of our lack of knowledge of the ultraviolet absorption spectra of the individual components, it was impossible to pick out the major component in these crude samples. To obviate this problem, we ordered chromatographically pure

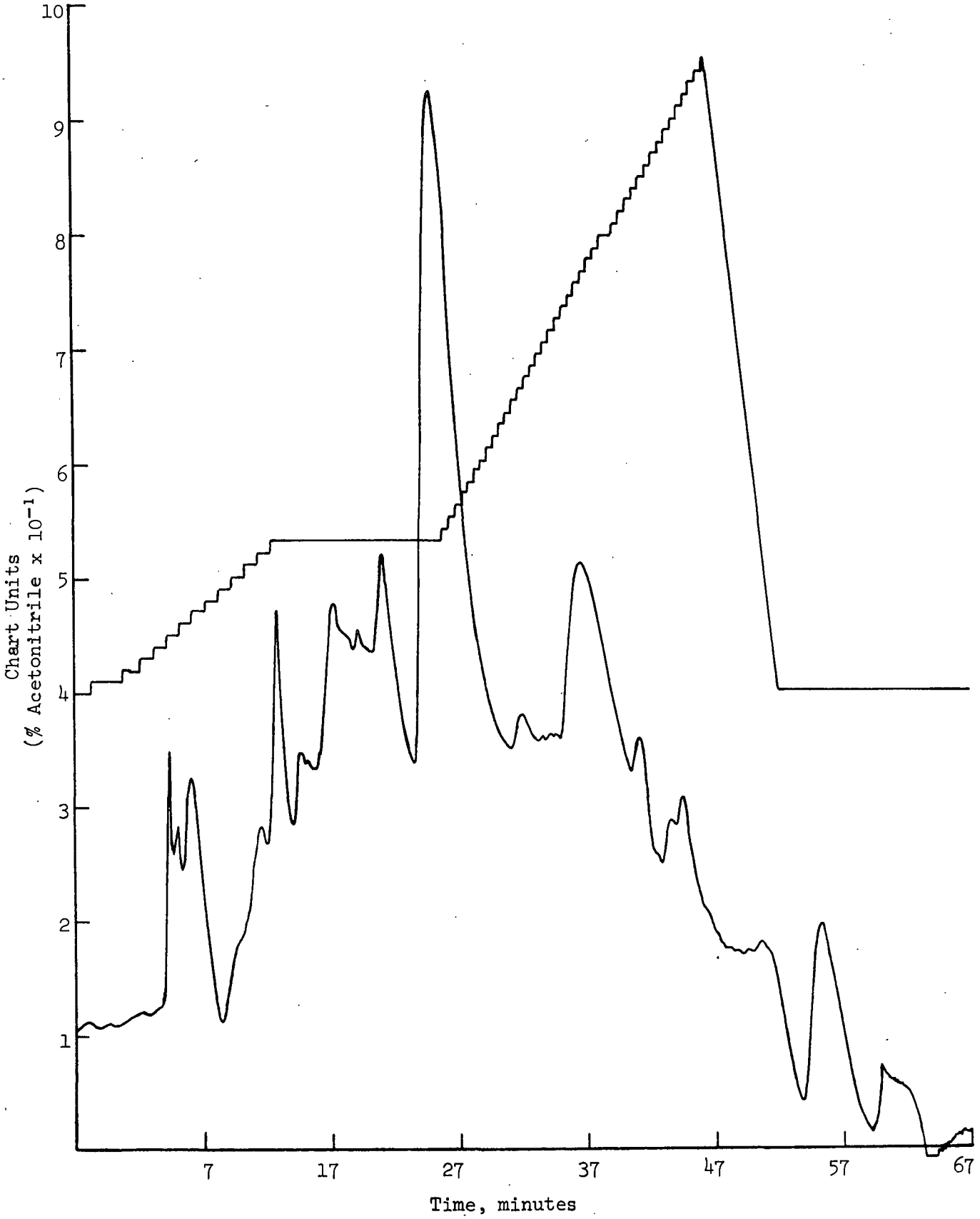

Figure 8. Gradient Elution Liquid Chromatogram on µBONDAPAK C-18 with Aqueous Acetonitrile of 2 Microliters Tall Oil Standard A at 60 ml/hr, 200 nm Detection and 10 mv Chart Span

samples of fatty and resin acids for reference purposes. Ultraviolet spectra and liquid chromatograms will be obtained for these compounds, and this information will be incorpoated in our next report.

Column Cleanup Experiments

In continued studies, it was noted that spurious peaks showed up from time to time, and it became evident that material was being deposited on our column, and the acetonitrile-water system moved some of these products so slowly that they appeared on chromatograms hours, days, or weeks later. Furthermore, it was obvious that valid chromtograms could not be obtained with this column until the impurities were removed. Since all of the components of our standard tall oil sample were extremely soluble in petroleum ether, this solvent appeared to be the solvent of choice for cleaning the column. Before attempting to clean the column, the experts at Waters Associates were consulted. We were informed that all investigators working with natural products always found materials in crude mixtures which could not be eluted from their columns with the solvent or solvent systems employed for analysis, and therefore, regular cleaning of columns was indicated. We were also told that our problem was somewhat worse than most because our good solvent, petroleum ether, was the least polar of all solvents, and our eluting solvents, acetonitrile and water (the only solvents compatible with our detecting wavelength of 200 nm), were extremely polar. Furthermore, our good solvent was insoluble in our eluting solvents. In order to prevent thermodynamic shock on our column, it was suggested that we go through a series of less polar and miscible solvents on the way to petroleum ether and then again on the way back to acetonitrile and water. Methanol and chloroform in that order were suggested on the way to petroleum ether, and in the reverse order on the way back to acetonitrile and water.

The column cleanup was initiated by eluting with 200 ml of methanol followed by 200 ml of chloroform, 400 ml of hexane, 200 ml of chloroform, 200 ml of methanol, and 200 ml of acetonitrile. All elutions were at the rate of 60 ml per hour. After the acetonitrile elution began, the detector was set at 200 nm, but with a span of 10 millivolts the recorder was off scale. In order to keep the record on the chart, it was necessary to raise the recorder span to 0.5 volt. In addition, the recorder trace was unsteady, even with the span set at 0.5 volt. The concentration of acetonitrile was gradually reduced with water with a negative gradient of 0.5 ml per minute, but the absorption at 200 nm was still exceptionally high at 3,500 units and very unsteady. After an hour at 10% acetonitrile, the concentration was raised to 50% acetonitrile at the rate of 0.5 ml per minute and maintained at 50% for several hours before allowing to stand overnight. During this time, the absorption had dropped to approximately 1,500 units with a very unsteady detector display and recorder trace. After standing overnight, elution was continued with 50% acetonitrile. After a few moments of elution, the absorption dropped to zero and remained there with a smooth trace and no unsteady display on the detector.

It appears that the high absorption and unsteady detector display were due to microdroplets of immiscible solvent in the acetonitrile-water mixtures, probably caused by absorption on the microparticulate column particles. During the last night of standing, these all dissolved or disappeared to leave a transparent solvent and a column ready for use.

EXPERIMENTS WITH TALL OIL STANDARD B

Tall oil standard B of a fatty acid-spiked kraft tall oil of loblolly pinewood was employed in several sets of experiments.

In order to determine whether faster flow rates and higher pressures would give better separations, 2-microliter samples of this standard solution were chromatographed on the Sil-X-I-C_{18} column with mixtures of acetonitrile and water at flow rates of 120 ml per hour. The detector was set at 200 nm. Isocratic and gradients were employed, but in all cases resolution was much poorer than analogous runs made at 60 ml per hour. In no instance was the gain in time worth the loss in resolution.

EXPERIMENTS WITH VYDAC RP COLUMN

We evaluated the VYDAC RP octadecyl silica reverse phase column, 2 mm ID and 50 cm in length, which came with our Varian equipment. Ostensibly, this column is the equivalent of the Perkin-Elmer Sil-X-I-C_{18} column, but results with this column were not quite as good as with the Perkin-Elmer column, and much poorer than with the Waters' μBONDAPAK C-18 column.

EXPERIMENTS WITH SILICA GEL COLUMN

According to the published literature on high performance liquid chromatography best universal results are usually obtained with silica gel column and elution with mixtures of lower alcohols and alkanes. We employed a Perkin-Elmer Sil-X-I column 4.6 mm in ID and 50 cm in length. Tall oil standard solution B was injected into this column and eluted with mixtures of isopropanol and hexane. The transparency of isopropanol was so poor in the 200-220 nm range that we could not find the compounds we were looking for. Pure hexane could be used at 205 nm, but the sensitivity was extremely low because we were pushing our detector to the limit of its base line capability.

Many wiggles appeared in the chromatograms indicating little peaks. We ultimately gave up on this type of column with our present detection equipment, although the chromatograms suggested that good separation of components had taken place on the column. These studies demonstrate that a universal type of detector is necessary if advantage is to be taken of the capability of silica gel columns with their extreme resolving power.

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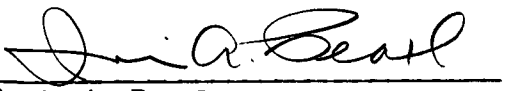

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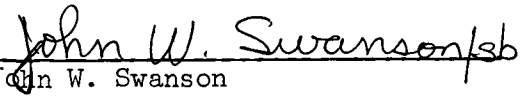

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